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Effect of Minor Alloying Elements on Corrosion Resistance of Al-Zn-Mg Alloy Welds[†]

Toshio ENJO* Toshio KURODA** and Shinya KANAMITSU***

Abstract

An investigation has been made of the effect of minor alloying elements on the corrosion resistance of Al-Zn-Mg alloy welds using a commercial Al-Zn-Mg alloy (7N01) and four kinds of Al-Zn-Mg alloys separately added 0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn and 0.2%Cr by means of the pitting potential of anodic polarization curve and electrical resistivity measurement.

The pitting potential in anodic polarization curve was related to the resistivity showing the solution of the minor alloy in the matrix rather than the weight percent of minor alloying addition.

The addition of 0.05%Ti to the Al-Zn-Mg alloy hardly shows the increase of the resistivity, and hardly affects the age hardening characteristics and pitting potential. The addition of 0.2%Fe-0.1%Si to the alloy hardly shows the increase of the resistivity, and hardly affects the pitting potential, but markedly affects the age hardening characteristics at 120°C.

The addition of 0.5%Mn to the alloy causes the markedly increase of the resistivity, and markedly causes the increase of the pitting potential for aged specimen but hardly affects the age hardening at 120°C. The addition of 0.2%Cr to the alloy affects both age hardening characteristics and the pitting potential. The age hardening at 120°C hardly occurs by the addition of Cr, but the pitting potential is improved.

The pitting potential depends on not only the amount of minor alloying elements but also the solution treatment temperature. As the relatively insoluble compounds is fairly solutionized in the matrix at 560°C solution temperature, the solute concentration of Cr increases in the matrix, and then the pitting potential increases and becomes more noble.

KEY WORDS: (Pitting Potential) (Breakdown Potential) (Corrosion) (Anodic Polarization) (Al-Zn-Mg Alloy) (Electrical Resistivity) (Minor Alloying Elements)

1. Introduction

Weldable Al-Zn-Mg alloys have been widely used for various structures. The alloy has a high strength, but has also a high susceptibility to stress corrosion cracking and corrosion.^{1)–5)}

The minor elements such as Cr, Mn, so on are added to the Al-Zn-Mg alloy, in order to improve the corrosion resistance and inhibit the grain growth and the stress corrosion cracking. The relatively insoluble compounds by various additions of minor alloying elements such as Al₁₈Cr₂Mg₃, Al₁₂Fe₃Si, Al₁₂Mn₃Si, so on, are formed during homogenization and solution treatment^{6),7)}. The compounds also inhibit the grain growth and affect the age hardening for commercial Al-Zn-Mg alloy.⁸⁾ However, the effect of each minor element has not been clearly made yet. It is important to make clear the effect of each

minor element for the development of new Al-Zn-Mg alloy.

The purpose of this paper is to present the effect of minor alloying elements on the corrosion resistance of commercial Al-Zn-Mg alloy using electrical resistivity measurement and electrochemical measurement.

2. Experimental Procedures

The materials used are commercial Al-Zn-Mg alloy and four kinds of Al-Zn-Mg alloys separately added 0.2%Cr, 0.5%Mn, 0.05%Ti and 0.2%Fe-0.1%Si to the alloy. The chemical compositions are shown in Table 1. The four kinds of alloys were casted. The cast ingots of each Al-Zn-Mg alloy were homogenized 24 hrs at 450°C, scalped and hot rolled to 10mm slabs at 300 to 400°C. The 10mm slabs were then cold rolled with intermediate anneals to

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Table 1 Chemical compositions of materials used (wt%).

Materials	Zn	Mg	Cu	Si	Fe	Mn	Cr	Ti	Zr	Al
7N01	4.58	1.15	tr.	0.08	0.16	0.45	0.21	0.05	0.2	Bal.
Al-Zn-Mg	5.82	1.48	tr.	0.01	0.03	tr.	tr.	tr.	tr.	Bal.
Al-Zn-Mg-Ti	5.48	1.44	tr.	0.01	0.02	tr.	tr.	0.05	tr.	Bal.
Al-Zn-Mg-Fe-Si	5.47	1.50	tr.	0.12	0.19	tr.	tr.	tr.	tr.	Bal.
Al-Zn-Mg-Mn	5.74	1.43	tr.	0.01	0.03	0.52	tr.	tr.	tr.	Bal.
Al-Zn-Mg-Cr	5.65	1.50	tr.	0.02	0.04	tr.	0.18	tr.	tr.	Bal.

the 11 mm thickness. The specimens were solution-treated at 380°C and 560°C for 2 hrs, water-quenched, and then aged at room temperature for 30 days and aged at 120°C for 50 hrs.

The heat treatments of the specimens were made in salt bath for the solution treatment at 380°C and 560°C, and in silicone oil bath for the aging treatment at 120°C. The each temperature was controlled to within $\pm 2^\circ\text{C}$.

The solution or precipitation behavior of the relatively insoluble compounds in the alloy was studied using electrical resistivity measurement⁸⁾. The thin plates for resistivity measurement were cut into strips 35 mm long, 2 mm wide and 0.5 mm thick, using electric discharge machine. The resistivity measurement were made in liquid nitrogen temperature by conventional potentiometric method.

The electrochemical measurement were made in order to evaluate the corrosion resistance. Anodic polarization curves showing the relation of potential to current density, were developed for each specimen. Each specimen was polished mechanically, first on 1500 grit emery paper, and finally on a cloth with 1 micron grain diamond abrasive. And the specimen was rinsed in deionized water, degreased in acetone, and then masked along its edges with stop-off lacquer prior to testing.

Each curve was developed by anodically polarizing a specimen from its free corrosion potential to a potential above its pitting potential. Potential/current curves were recorded at potential scan rate of 20 mV/min. The potential and current were also measured automatically using a computer which was connected with a potentiostat using G.P.I.B. interface. The pitting potential was exactly decided on the basis of the digital data from a computer.

The electrolyte used was 1M NaCl solution which was deaerated by bubbling argon through the solution for at least 30 min. before immersing the specimen. The pH of the electrolyte was 11.0.

3. Results and Discussion

3.1 Anodic polarization characteristics of commercial Al-Zn-Mg alloy

Figure 1 shows anodic polarization curves of commercial Al-Zn-Mg alloy (7N01), which were solution-

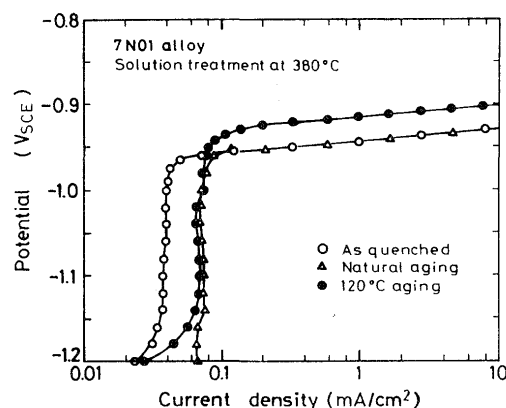


Fig. 1 Anodic polarization curves of commercial Al-Zn-Mg alloy (7N01), which were solution-treated at 380°C for 2 hrs water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

treated at 380°C for 2 hrs, water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

In all cases, the specimens showed a passive range, where no attack was observed. But as the potential was increased to the critical potential, there was a marked increase in the current, and pitting was then detected on the surface. The existence of critical potential was reported by various authors⁹⁾⁻¹²⁾, and the pitting potential was also named as breakdown potential¹³⁾.

The most appropriate way of distinguishing between the anodic polarization curves is to define each of these curves in terms of initial and final pitting potentials and the values of these potentials.

For the as-quenched specimen, a single breakdown is found, occurring at $-961\text{ mV}_{\text{SCE}}$ (Saturated Calomel Electrode) followed by a rapid rise in current density. The region between the corrosion potential ($-1300\text{ mV}_{\text{SCE}}$) and the pitting potential ($-961\text{ mV}_{\text{SCE}}$) is a region of passivity, although the current is too low to be plotted in Fig. 1.

The pitting potential of natural aging is almost same value as with the as-quenched specimen. But the potential is $-938\text{ mV}_{\text{SCE}}$, the value becomes more noble than that of as-quenched specimen.

Figure 2 shows anodic polarization curves of commercial Al-Zn-Mg alloy (7N01), which were solution-treated at 560°C for 2 hrs, water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

The anodic polarization curve shows the same tendency as with that of 380°C solution treatment.

Such a change in the pitting potential depends on the aging treatment, namely, the microstructure. The microstructure change by artificial aging treatment depends on the minor alloying elements. But in a commercial Al-Zn-Mg alloy, various minor elements are included.

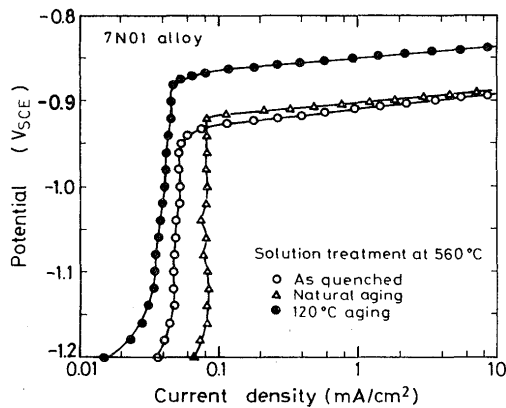


Fig. 2 Anodic polarization curves of commercial Al-Zn-Mg alloy (7N01), which were solution-treated at 560°C for 2 hrs water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

3.2 Effect of minor alloying elements on resistivity change by solution treatment

Generally, the solid solution of minor elements such as Cr, Mn so on in the matrix causes the increase of resistivity.

The relatively insoluble compounds are formed by minor elements in the alloy⁸⁾, and the resistivity change occurs due to the solution or precipitation of the compounds. As the compounds are solutionized in the matrix, the resistivity increases. But as the compounds precipitate more, the resistivity decreases, because of the decrease of the concentration of the solute atom in the aluminum matrix.

Figure 3 shows the relation between resistivity change and minor alloying elements, as the specimens were solution-treated at 560°C and 380°C for 2 hrs, water quenched.

The resistivity of Al-Zn-Mg alloy was 1.72 $\mu\Omega\text{cm}$. The resistivity change is hardly recognized. It means that precipitates such as G.P. zones, η' precipitates and η phase are solutionized, that is, Zn and Mg are solutionized in the matrix by the solution treatment above 380°C. In the case of the alloy with 0.05%Ti or 0.2%Fe-0.1%Si, the resis-

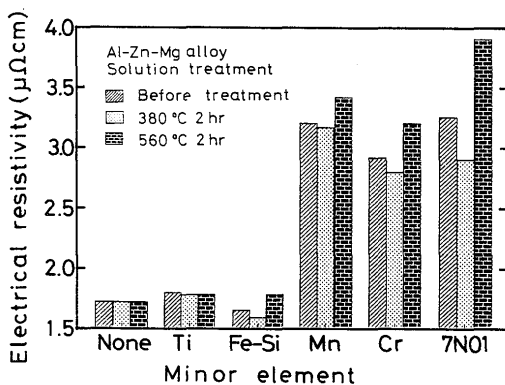


Fig. 3 Effect of minor alloying elements (0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn, 0.2%Cr) on resistivity change as the specimens were solution-treated at 560°C and 380°C for 2 hrs, water quenched.

tivity change by solution treatment hardly occurs.

On the other hand, the addition of 0.5%Mn or 0.2%Cr to the Al-Zn-Mg alloy takes place the marked increase of the resistivity.

The resistivity of the alloy with 0.5%Mn increases more by 560°C solution treatment. It means that the relatively insoluble compounds were solutionized more by 560°C treatment.

In the case of the alloy with 0.2%Cr, the resistivity decreases by the 380°C solution treatment, which means that the compounds such as $\text{Al}_{18}\text{Cr}_2\text{Mg}_3$ precipitate more. The resistivity increases by the 560°C solution treatment, which means that the compounds slightly solutionize to the matrix.

For the commercial Al-Zn-Mg alloy (7N01), the change in the resistivity is similar to that of the alloy with Cr and Mn.

Consequently, the resistivity change of the commercial Al-Zn-Mg alloy (7N01) by solution temperature is concluded to occur due to the solution or precipitation of the compounds with Cr and Mn.

3.3 Effect of minor alloying elements on the age hardening characteristics

Figure 4 shows the relation between the hardness by aging and minor additional elements, as the specimens were solution treated at 560°C and 380°C for 2 hrs, water quenched, and then aged at room temperature for 30 days.

The hardness of the Al-Zn-Mg alloy with minor elements is hardly affected by the solution temperature, except that the addition of Mn causes fairly the increase of hardness. Consequently, the minor additional elements hardly affect the age hardening characteristics by the natural aging at room temperature.

Figure 5 shows the relation between the hardness by aging and minor alloying elements, as the specimens were solution treated at 560°C and 380°C for 2 hrs, water quenched, and then aged at 120°C for 50 hrs.

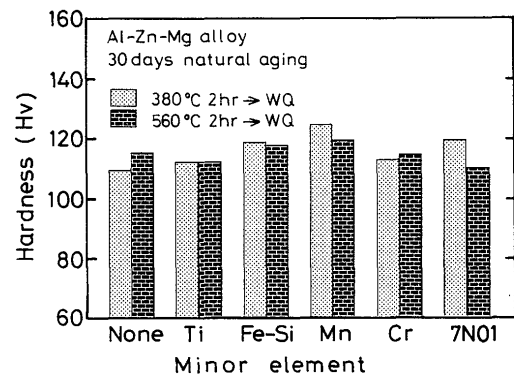


Fig. 4 Effect of minor alloying elements (0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn, 0.2%Cr) on hardness, as the specimens were solution-treated at 560°C and 380°C for 2 hrs, water quenched, and then aged at room temperature for 30 days.

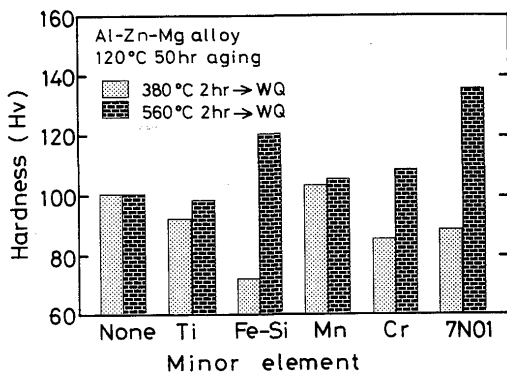


Fig. 5 Effect of minor alloying elements (0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn, 0.2%Cr) on hardness, as the specimens were solution-treated at 560°C and 380°C for 2 hrs, water quenched, and then aged at 120°C for 50 hr.

The hardness of the alloy with minor elements is affected by the solution temperature, though the hardness of the alloy without minor elements is hardly affected.

The hardness of the solution treatment at 560°C is higher than that of the 380°C solution treatment, except the alloy with Mn. It means that the precipitation of the relatively insoluble compounds by minor element inhibit the age hardening at 120°C. Especially, the addition of 0.2%Cr and 0.2%Fe-0.1%Si to the Al-Zn-Mg alloy affect the age hardening at 120°C.

Consequently, the age hardening characteristics at 120°C for the commercial Al-Zn-Mg alloy (7N01) is concluded to be affected by the minor alloying elements such as Cr and Fe-Si.

3.4 Effect of minor alloying elements on pitting potential

Figure 6 shows the relation between pitting potential and minor alloying elements in the Al-Zn-Mg alloy, as the specimens were solution-treated at 380°C for 2 hrs, water quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

In the case of the Al-Zn-Mg alloy without minor alloying elements, the pitting potential for the specimen aged at 120°C becomes fairly higher than that of as-quenched

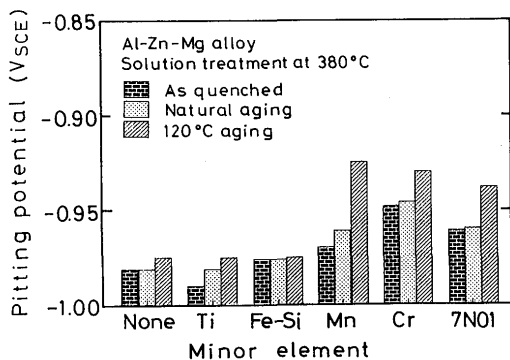


Fig. 6 Effect of minor alloying elements (0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn, 0.2%Cr) on pitting potential as the specimens were solution-treated at 380°C for 2 hrs, water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

specimen.

For the alloy with 0.05%Ti, the pitting potential becomes higher by each aging treatment.

In the case of the alloy with 0.2%Fe-0.1%Si, the pitting potential is hardly affected by the aging treatment.

On the other hand, the pitting potential of the alloy with 0.5%Mn and 0.2%Cr is markedly affected by the aging treatment. The addition of Mn or Cr causes the increase of the pitting potential by 120°C aging.

The change in the pitting potential by aging treatment for the commercial Al-Zn-Mg alloy (7N01) is similar to those of the alloy with Mn and Cr.

Consequently, the pitting potential of the commercial Al-Zn-Mg alloy (7N01) is considered to depend on the addition of Mn and Cr.

Figure 7 shows the relation between pitting potential and minor alloy elements in the Al-Zn-Mg alloy, as the specimens were solution-treated at 560°C for 2 hrs, water quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

The pitting potential is hardly affected by minor alloying elements such as 0.05%Ti and 0.2%Fe-0.1%Si, but affected by the alloying elements of 0.5%Mn and 0.2%Cr.

In comparison of Fig. 6 and Fig. 7, the addition of Ti and Fe-Si to the Al-Zn-Mg alloy hardly affects the pitting potential, independent of the solution treatment temperature.

In the case of the as-quenched specimen, the increase of pitting potential is mainly caused by addition of Cr.

Table 2 is summarized the pitting potentials obtained in this investigation.

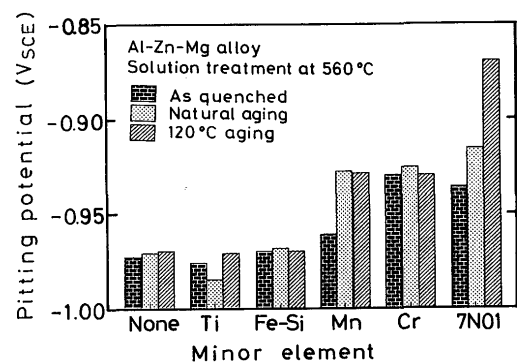


Fig. 7 Effect of minor alloying elements (0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn, 0.2%Cr) on pitting potential as the specimens were solution-treated at 560°C for 2 hrs, water-quenched, and then aged at room temperature for 30 days or aged at 120°C for 50 hrs.

3.5 Effect of minor alloying treatment and aging treatment on pitting potential

Aluminum is a very basic metal with a reversible potential at approximately $-1900 \text{ mV}_{\text{SCE}}$, but it is very easily passivated so that over a wide range of potentials the current density is very low. Aluminum will also pit in a NaCl

Table 2 Pitting potentials obtained in this study.

Minor alloying additions	Pitting potential (mV)		
	As quenched	Natural aging	120°C aging
Solution treatment at 380°C			
Al-5%Zn-1.5%Mg	-981	-981	-975
Al-5%Zn-1.5%Mg-0.05%Ti	-990	-981	-975
Al-5%Zn-1.5%Mg-0.2%Fe-0.1%Si	-976	-976	-975
Al-5%Zn-1.5%Mg-0.5%Mn	-970	-961	-925
Al-5%Zn-1.5%Mg-0.2%Cr	-948	-946	-930
Commercial 7N01 alloy	-961	-960	-938
Solution treatment at 560°C			
Al-5%Zn-1.5%Mg	-973	-971	-970
Al-5%Zn-1.5%Mg-0.05%Ti	-976	-985	-971
Al-5%Zn-1.5%Mg-0.2%Fe-0.1%Si	-970	-968	-970
Al-5%Zn-1.5%Mg-0.5%Mn	-961	-928	-929
Al-5%Zn-1.5%Mg-0.2%Cr	-930	-926	-930
Commercial 7N01 alloy	-936	-916	-870

solution. The pitting potential of high purity aluminum is near $-770 \text{ mV}_{\text{SCE}}$. The current density rises rapidly at this potential.

A 5%Zn and a 1.5%Mg has been added to the Al-Zn-Mg alloy. Zinc greatly reduces the pitting potential⁹⁾. Therefore, its addition will reduce the passive range usually observed in aluminum alloys. The addition of 5%Zn reduce $200 \text{ mV}_{\text{SCE}}$ ⁹⁾. Magnesium additions have comparatively little effect on the pitting potential up to 5 percent. It is also important to note that the most common grain boundary precipitate MgZn_2 is easily dissolved at potentials above $-860 \text{ mV}_{\text{SHE}}$, ($-1100 \text{ mV}_{\text{SCE}}$)¹⁴⁾.

Table 3 indicates electrode potentials of aluminum solid solutions and constituents.¹⁴⁾ Mg, Zn and MgZn_2 are

Table 3 Electrode potentials of aluminum solid solutions and constituents¹⁴⁾.

Phase	Potential, V_{SCE}
Mg	-1.73
Zn	-1.10
Mg_2Al_3	-1.24
Al + 4 MgZn_2	-1.07
Al + 4 Zn	-1.05
MgZn_2	-1.05
CuMgAl_2	-1.00
Al + 1 Zn	-0.96
Al + 7 Mg	-0.89
Al + 5 Mg	-0.88
Al + 3 Mg	-0.87
MnAl_6	-0.85
99.95 Al	-0.85
Al + 1 Mg_2Si	-0.83
Al + 1 Si	-0.81
Al + 2 Cu	-0.75
CuAl_2	-0.73
Al + 4 Cu	-0.69
FeAl_3	-0.56
NiAl_3	-0.52
Si	-0.26
Cu	-0.20

very active, but Si, Fe, and Mn are noble, though the effect of Cr has not been known yet. Consequently, the minor alloying additions to the Al-Zn-Mg alloy in present study are considered to cause the increase of pitting potential.

As shown in Fig. 6 and Fig. 7, the pitting potential increases by minor alloying additions.

Then, from the results of Fig. 3 and Fig. 6, Fig. 7, the relation between resistivity of the Al-Zn-Mg alloy with minor alloying elements and pitting potential is shown in Fig. 8.

In the case of as-quenched specimen shown in Fig. 8-(a), the pitting potential increases with increasing the resistivity, independent of the kinds of minor alloying. For the addition of Cr and Mn, the resistivity is changed by the solution, or precipitation of relatively insoluble compounds, as if the amount of minor alloying additions were same.

The pitting potential is not only depends on the solution amount of minor alloying elements in the Al-Zn-Mg alloy but also depends on the solution treatment temperature. Consequently, the minor alloying is considerably solutionized at bond area for welding, the pitting potential becomes more noble than that of base metal, and the corrosion resistance seems to be high.

As shown in Fig. 8-(b), and Fig. 8-(c), the pitting potential increases with increasing the resistivity, for natural aging treatment for 30 days and artificial aging treatment at 120°C .

Figure 9 shows the relation between pitting potential and the resistivity for as-quenched specimen, natural aging specimen and the specimen of artificial aging at 120°C .

The amount of minor alloying elements to the Al-Zn-Mg alloy becomes higher, the increase of the pitting potential becomes higher. G.P. zones precipitate at natural aging, and G.P. zones, η' precipitates and η phase precipitate for artificial aging⁸⁾.

These precipitates causes the increase in the pitting

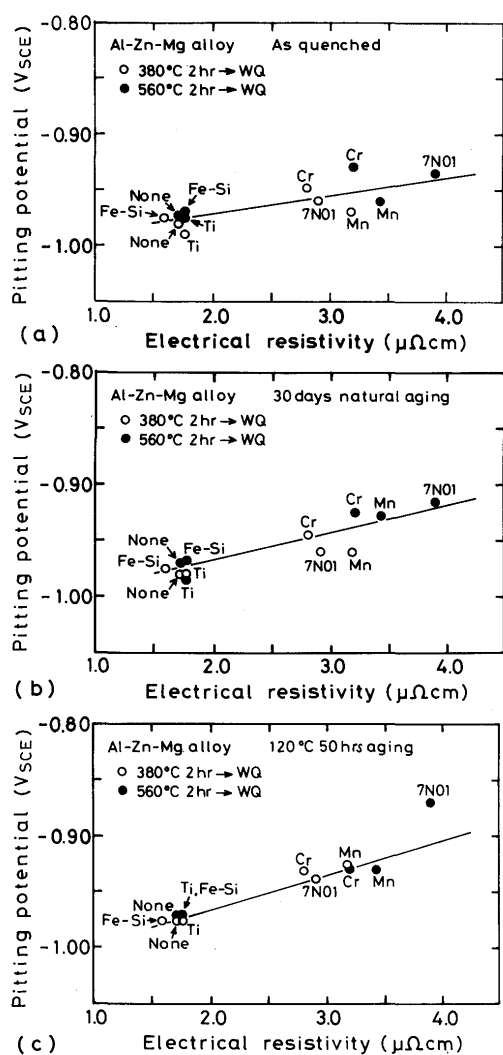


Fig. 8 Effect of resistivity and minor alloying elements on pitting potential for as-quenched specimens(a), natural aged specimens(b) and artificial aged specimens(c).

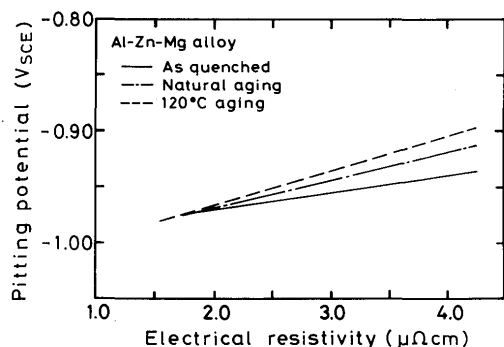


Fig. 9 Effect of aging treatment on pitting potential.

potential, though $MgZn_2$ precipitates at the grain boundary and in grain for artificial aging. Therefore, the pitting potential indicates that the pitting occurs not at the precipitates such as $MgZn_2$ but in the matrix. It is concluded that the pitting potential depends on the concentration of solute atom in the aluminum matrix.

Consequently, the minor alloying elements affect not

only age hardening characteristics but also pitting potential.

4. Conclusions

An investigation has been made of the effect of minor alloying elements on the corrosion resistance of Al-Zn-Mg alloy welds using a commercial Al-Zn-Mg alloy (7N01) and four kinds of Al-Zn-Mg alloys separately added 0.05%Ti, 0.2%Fe-0.1%Si, 0.5%Mn and 0.2%Cr.

The results obtained in this investigation are summarized as follows.

- 1) The pitting potential in anodic polarization curve was related to the resistivity showing the solution of the minor alloy in the matrix rather than the weight percent of minor alloying addition.
- 2) The addition of 0.05%Ti to the Al-Zn-Mg alloy hardly causes the increase of the resistivity, and hardly affects the age hardening characteristics and pitting potential.
- 3) The addition of 0.2%Fe-0.1%Si to the alloy hardly causes the increase of the resistivity, but hardly affects the pitting potential, but markedly affects the age hardening characteristics at 120°C.
- 4) The addition of 0.5%Mn to the alloy causes the markedly increase of the resistivity, and markedly causes the increase of the pitting potential for aged specimen but hardly affects the hardening at 120°C.
- 5) The addition of 0.2%Cr to the alloy affects both age hardening characteristics and the pitting potential. The age hardening at 120°C hardly occurs by the addition of Cr, but the pitting potential is improved.
- 6) The pitting potential depends on not only the amount of minor alloying elements but also the solution treatment temperature. As the relatively insoluble compounds is fairly solutionized in the matrix at 560°C solution temperature, the solute concentration of Cr increases in the matrix, and then the pitting potential increases and becomes more noble.
- 7) The age hardening characteristics at 120°C and the change in the pitting potential is related to the addition of Cr and Mn for commercial Al-Zn-Mg alloy (7N01).

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